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Reactions of tetracyanoethylene with dimethyl/arylhydrazines and arylamines

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Experimental section

All reagents were obtained from commercial suppliers and used without further purification. The progress of the reactions and the purity of the products were monitored using thin-layer chromatography (TLC) on Sorbfil plates, with visualization under UV light, iodine vapor treatment, or heating. The melting and decomposition temperatures were determined using the Optibelt MPA 100 device. Infrared (IR) spectra were recorded on a Fourier transform spectrometer FSM-1202 for samples dissolved in Nujol. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$ with tetramethylsilane (TMS) as the internal standard on a Bruker AVANCE 400 WB spectrometer operating at frequencies of 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C.

HRMS mass spectra of **2a**,**b**, **5a-c** and **6** were acquired using the quadrupole time-of-flight (t, qTOF) AB Sciex Triple TOF 5600 mass spectrometer (AB SCIEX PTE. Ltd., Singapore) equipped with a turbo-ion spray source. The nebulizer gas used was nitrogen, and the ionization polarity was positive (+). The needle voltage was set at 5500 V. The spectra were recorded in the time-of-flight mass spectrometry (TOF MS) mode with a collision energy of 10 eV, declustering potential of 100 eV, and a resolution exceeding 30,000 full-width half-maximum. Sample solutions with an analyte concentration of 5 μmol/L were prepared by dissolving the test compounds in methanol (hypergrade for LC-MS, Merck).

The components of the reaction mixture were analyzed using gas chromatography with a nitrogen-phosphorus detector (AFD) and a polymer sorbent Chromosorb from Alltech Associates. Chromatograms were processed and quantified using the "ECOCHROME" software and hardware system for registration and calculation of chromatograms (TU 5E2.148.003). Gas retention times were measured using an SDSpr. 1-2-000 stopwatch (GOST 5072-79).

5-Amino-1-methyl-1*H*-pyrazole-3,4-dicarbonitrile (3a). To a solution of tetracyanoethylene **1** (2 mmol) in methanol (2 ml), 1,1-dimethylhydrazine **2a** (2 mmol) was added. The mixture was kept at an ambient temperature for 96 hours. The precipitate was filtered out, washed with cooled methanol (2 ml). The yield is 91%, m. p. 233-235 °C (MeOH). IR spectrum, ν, cm^{-1}: 3410, 3341, 3251 (NH_2), 2252, 2223 (C≡N), 1662, 1591 (C=C). ^1H NMR, δ, ppm.: 7.19 (s, 2H, NH_2), 3.61 (s, 3H, CH_3). ^{13}C NMR spectrum, δ_c, ppm: 152.85 (C^4), 124.22 (C^2), 112.93 (C^7N^9), 112.90 (C^8N^{10}), 76.63 (C^3), 36.50 (CH_3^6). Found, %: C 49.15; H 3.54; N 41.31. $C_6H_5N_5$. Calculated, %: C 48.98; H 3.43; N 47.60.

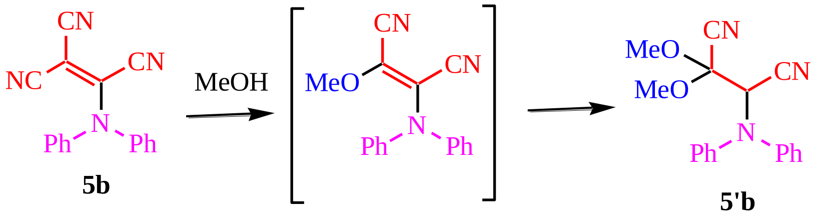
5-Amino-1-(pyridin-2-yl)-1*H*-pyrazole-3,4-dicarbonitrile (3b). To a solution of *N*-(2-pyridyl)hydrazine **2b** (2 mmol) in ethanol (3 ml), tetracyanoethylene **1** (2 mmol) in ethanol (3 ml) was added. The mixture was stirred for 3 h (TLC control), kept at ambient temperature over 12 hours and cooled. The precipitate was filtered off and washed with cold ethanol (2 ml). The yield is 89%, m.p. 183-185 °C (EtOH). IR spectrum, ν, cm^{-1}: 3290, 3200 (NH_2), 2227 (C≡N), 1586 (C=C). ^1H NMR , δ, ppm.: 8.52 s (2H, NH_2), 8.50 – 8.44 m (1H, CH^{13}), 8.13 – 7.94 m (1H, CH^{15}), 7.81 dt (,*J* = 8.4, 0.9 Hz, 1H, CH^{16}), 7.55 – 7.33 m (1H, CH^{14}). ^{13}C NMR, δ_c, ppm: 152.98 (C^4), 152.16 (C^6), 147.26 (CH^{13}), 140.31 (CH^{15}), 126.39 (C^2), 122.72 (CH^{14}), 113.85 (C^7N^9), 111.76 (C^8N^{10}). Found, %: C 57,22; H 3,14; N 39,64. $C_{10}H_6N_6$. Calculated, %: C 57.14; H 2.88; N 39.98.

Ethyl 4-[(1,2,2-tricyanovinyl)amino]benzoate (5a). To a solution of ethyl 4-amino-benzoate (2 mmol) **4a** in methanol (3 ml), tetracyanoethylene **1** (2 mmol) in methanol (3 ml) was added. The mixture was stirred for 30 min, then the solvent was distilled off. A yellow crystalline residue was washed with cold 1:1 ethyl acetate-hexane mixture (2 ml). The yield is 71%, m. p. 170-172 ºC (MeOH). IR spectrum, v, cm^{-1}: 3278 (NH), 2257, 2226 (C≡N), 1653 (C=O), 1462 (C=C). ^1H NMR, δ, ppm.: 8.10 – 7.91 (m, 2H, CH^{14}, CH^{12}), 7.53 – 7.33 (m, 2H, CH^{15}, CH^{11}), 5.69 (s, 1H, NH), 4.31 (q, *J* = 7.1 Hz, 2H, CH_2^{19}), 1.32 (t, *J* = 7.1 Hz, 3H, CH_3^{20}). ^{13}C NMR, δ_c, ppm: 165.01(C^{16}=O), 139.41 (C^1), 130.16 (CH^{14}, CH^{12}), 127.88 (C^{13}), 123.48 (CH^{15}, CH^{11}), 115.43 (C^5N^{10}), 114.62 (C^7N^8), 111.17 (C^6N^9), 60.81 (CH_2^{19}), 14.11 (CH_3^{20}). Found, %: C 62.98; H 3.56; N 21.25. $C_{14}H_{10}N_4O_2$. Calculated, %: C 63.15; H 3.79; N 21.04.

2-(Diphenylamino)ethene-1,1,2-tricarbonitrile (5b): Tetracyanoethylene **1** (2 mmol) dissolved in 2-propanol (3 ml) was added to a solution of diphenylamine **4b** (2 mmol) in 2-propanol (5 ml), and this was stirred for 25 min. A pink discoloration from green and then to burgundy was observed. The solution was evaporated, the resin-like precipitate was recrystallized after treatment the solution with aluminum oxide and activated carbon. A purple powder precipitation was observed. Yield: 16%, m. p. 162-163ºC. IR spectrum, v, cm^{-1}: 3196 (NH), 2226 (C≡N), 1653 (NH) , 1462 (Ar). ^1H NMR, δ, ppm.: 6.77 (t, *J* = 7.7 Hz, 4H, CH^{12},

CH^{10}, CH^4, CH^1), 6.62 (d, *J* = 7.9 Hz, 4H, CH^{13}, CH^9, CH^6, CH^4), 6.36 (t, *J* = 7.3 Hz, 2H, CH^{11}, CH^2). ^{13}C NMR, δ_c, ppm: 151.94 (C^{14}), 143.43 (C^8, C^5), 129.15 (CH^{12}, CH^{10}, CH^3, CH^1), 119.66 (CH^{11}, CH^2), 116.73 (CH^{13}, CH^9, CH^6, CH^4), 114.76 ($C^{18}N^{19}$, $C^{16}N^{17}$), 114.18 ($C^{20}N^{21}$), 57.84 (C^{15}). Mass spectrum, *m/z*: $[M + H]^+$ 308.1400 (calculated for $[C_{18}H_{17}N_3O_2]^+$ 308.1394). Found, %: C, 75.49; H, 3.68; N, 20.65. $C_{17}H_{10}N_4$: calculated, %: C, 75.54; H, 3.73; N, 20.73.

When compound **5b** was dissolved in MeOH, during the recording mass spectrum it may have undergone transformation at the ionization point outlined in Scheme S1, so the spectrum was registered for structure **5'b**. Mass spectrum, *m/z*: Calcd. $C_{18}H_{18}N_3O_2$: 308.1399 $[M+1]^+$, Found: 308.1400. The sample taken at the spectrometer probe was also subjected to elemental analysis which approached the structure **5'b**. Found, %: C 70.25; H 5.43; N 13.79. $C_{18}H_{17}N_3O_2$: Calculated, %: C 70.34; H 5.58; N 13.67.



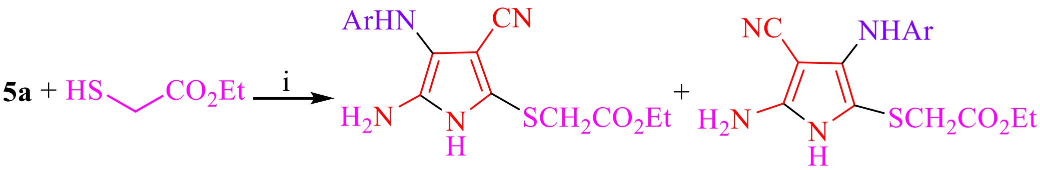
Scheme S1

2-[(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)amino]ethene-1,1,2-tricarbonitrile (5c) was prepared similarly to product **5a**. Yield: 50%, m.p. 232-233°C. IR spectrum, ν, cm^{-1}: 3177 (NH), 2218 (C≡N), 1636 (C=O). NMR spectrum ^{1}H, δ, ppm.: 7.08 (t, *J* = 7.6 Hz, 2H, CH^{16}, CH^{14}), 6.96 (t, *J* = 7.4 Hz, 1H, CH^{15}), 6.87 (d, *J* = 6.5 Hz, 2H, CH^{17}, CH^{13}), 3.25 (s, 1H, NH), 2.73 (s, 3H, CH_3^{10}), 1.84 (s, 3H, CH_3^{12}). NMR spectrum ^{13}C, δ_c, ppm: 160.40 (C^2=O), 143.39 (C^8), 134.31 (C^{10}), 129.60 (CH^{16}, CH^{14}), 127.81 (C^4), 126.14 (CH^{17}, CH^{13}), 125.26 (CH^{15}), 114.91 ($C^{20}N^{21}$, $C^{18}N^{19}$), 112.16 ($C^{22}N^{23}$), 103.23 (C^3), 60.30 (C^9), 34.94 (CH_3^{11}), 10.35 (CH_3^{12}). Mass spectrum, *m/z*: $[M + H]^+$ 305.1151 (calculated for $[C_{16}H_{12}N_6O]^+$ 305.1145). Found, %: C 63.16; H 3.91; N 27.63. $C_{16}H_{12}N_6O$. Calculated, %: C 63.15; H 3.97; N 27.62.

4-[*N*-(1,1,2,2-Tetracyanoethyl)-*N*-(1,2,2-tricyanovinyl)amino]phenyl acetate (6): To a solution of 4-acetoxyaniline **4d** (2 mmol) in 2-propanol (5 ml), tetracyanoethylene **1** (4 mmol) in 2-propanol (3 ml) was added. The mixture was stirred at room temperature for 25 min until the blue complex discoloration on the surface of the hydroquinone test occurred. The solvent was evaporated. The solid residue was washed with cold ethyl acetate-hexane mixture (2 ml). Yield: 40%, m. p. 148-149 °C. IR spectrum, ν, cm^{-1}: 3220 (NH), 2233 (C≡N), 1683 (C=O), 1159 (OCH_3). NMR spectrum ^{1}H, δ, ppm.: 7.69 – 7.47 m (2H, CH^4, CH^2), 7.12 – 6.92 m (2H, CH^5, CH^1), 3.98 s (1H, CH^{19}), 2.13 s (3H, CH_3). NMR spectrum ^{13}C, δ_c, ppm: 195.68 (C^9=O), 150.21

(C^{13}), 143.83 (C^6), 139.82 (CH^4, CH^2), 135.26 (CH^5, CH^1), 130.71 ($C^{21}N^{29}$), 129.66 ($C^{22}N^{28}$), 127.57 (C^3), 123.76 ($C^{20}N^{27}$, $C^{18}N^{26}$, $C^{17}N^{25}$, $C^{16}N^{24}$), 120.18 (C^{15}), 115.08 ($C^{14}N^{23}$), 60.54 (C^{12}), 27.01 ($CH_3{}^{10}$), 26.32 (CH^{19}). Mass spectrum, m/z: $[M + H]^+$ 381.0848 (calculated for $[C_{19}H_8N_8O_2]^+$ 381.0842) Found, %: C 60.85; H 2.05; N 29.24. $C_{19}H_8N_8O_2$. Calculated, %: C, 60.00; H, 2.12; N, 29.46.

Attempted reaction of compound **5a** *with ethyl 2-mercaptoacetate* (Scheme S2). A change in color of the reaction mixture was observed. Monitoring by TLC ($CHCl_3$/EtOAc, 1:1) revealed formation of two products with close R_f values in the ratio of ≈ 2.3:1. Unfortunately, due to the high solubility of the resulting compounds and the tarring of the reaction mixture when removing the solvent we failed to isolate the products with supposed structures **7** and **7'** (see Refs. 24 and 25 of the main text).



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Scheme S2 *Reagents and conditions:* i, MeOH, room temperature

Figure S1. ^{1}H NMR spectrum of **3a** (400 MHz, DMSO-d_6, 298 K)

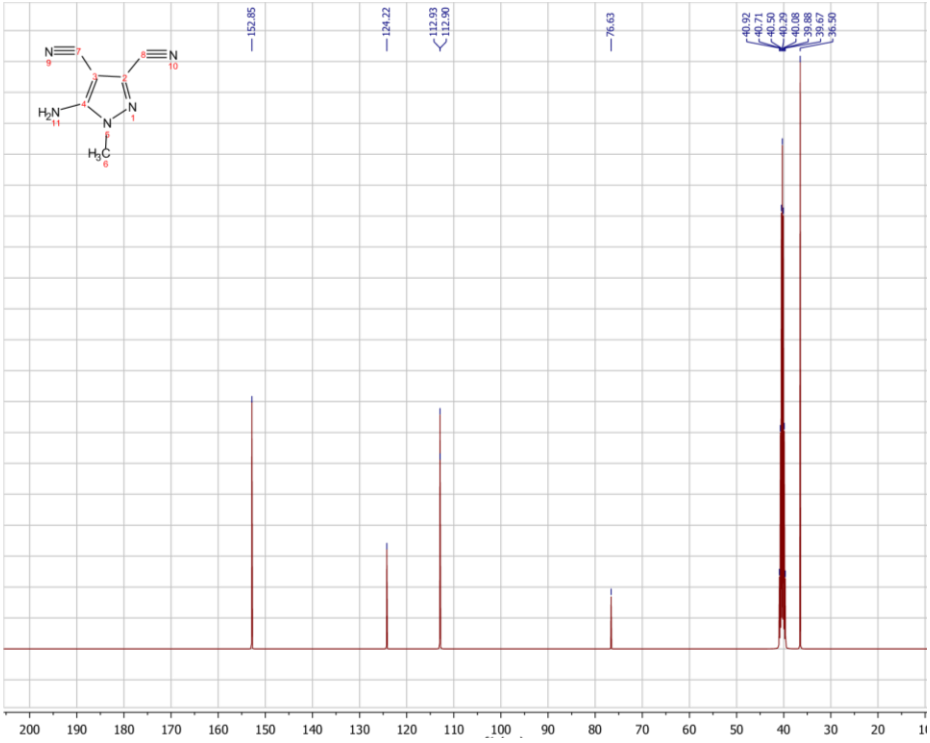

Figure S2. ^{13}C NMR spectrum of **3a** (100 MHz, DMSO-d$_6$, 298 K)

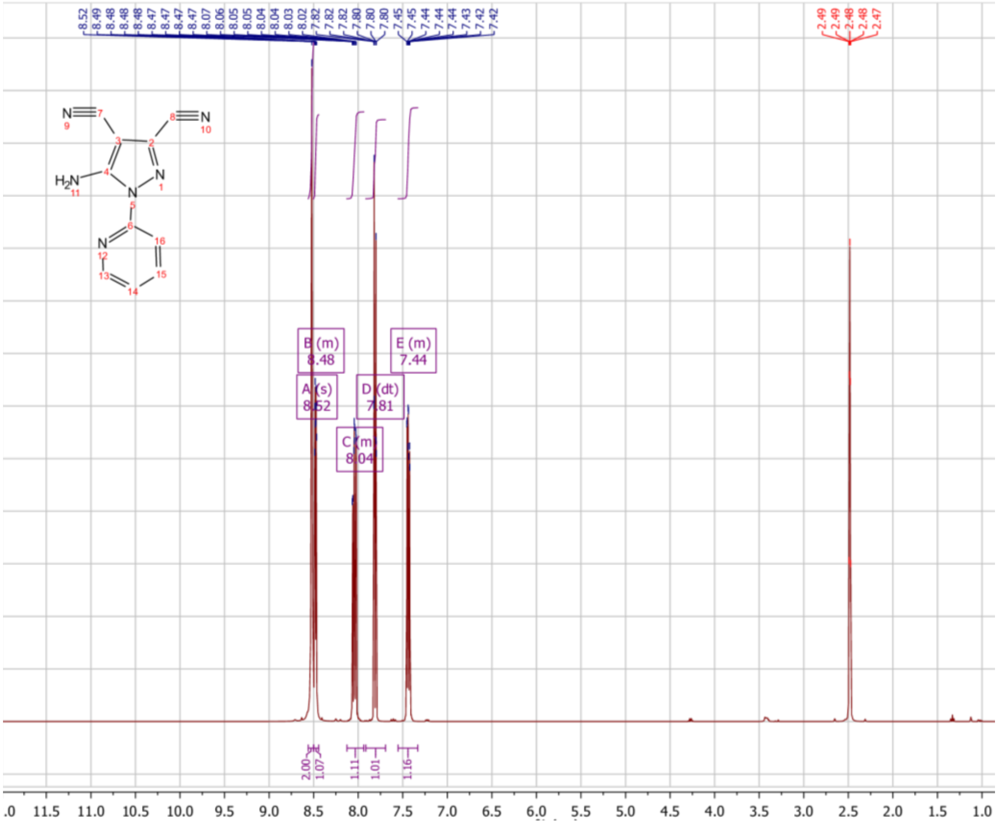

Figure S3. ^{1}H NMR spectrum of **3b** (400 MHz, DMSO-d$_6$, 298 K)

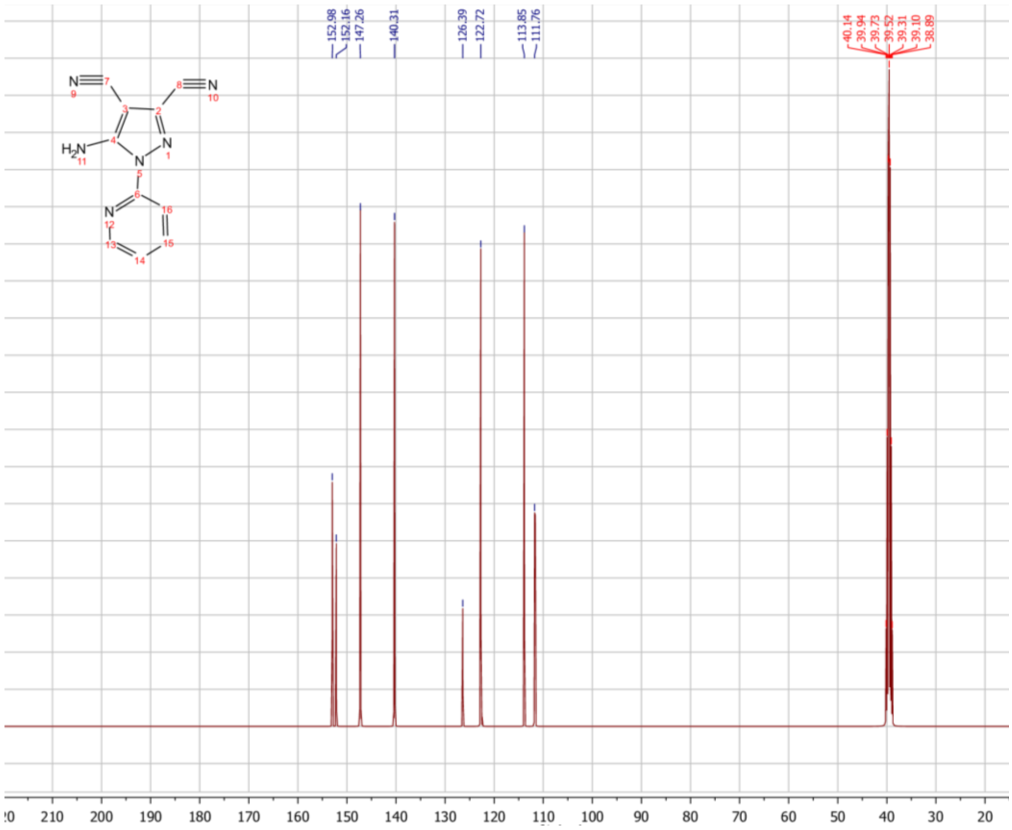

Figure S4. ^{13}C NMR spectrum of **3b** (100 MHz, DMSO-d$_6$, 298 K)

Figure S5. ^{1}H NMR spectrum of **5a** (400 MHz, DMSO-d$_6$, 298 K)

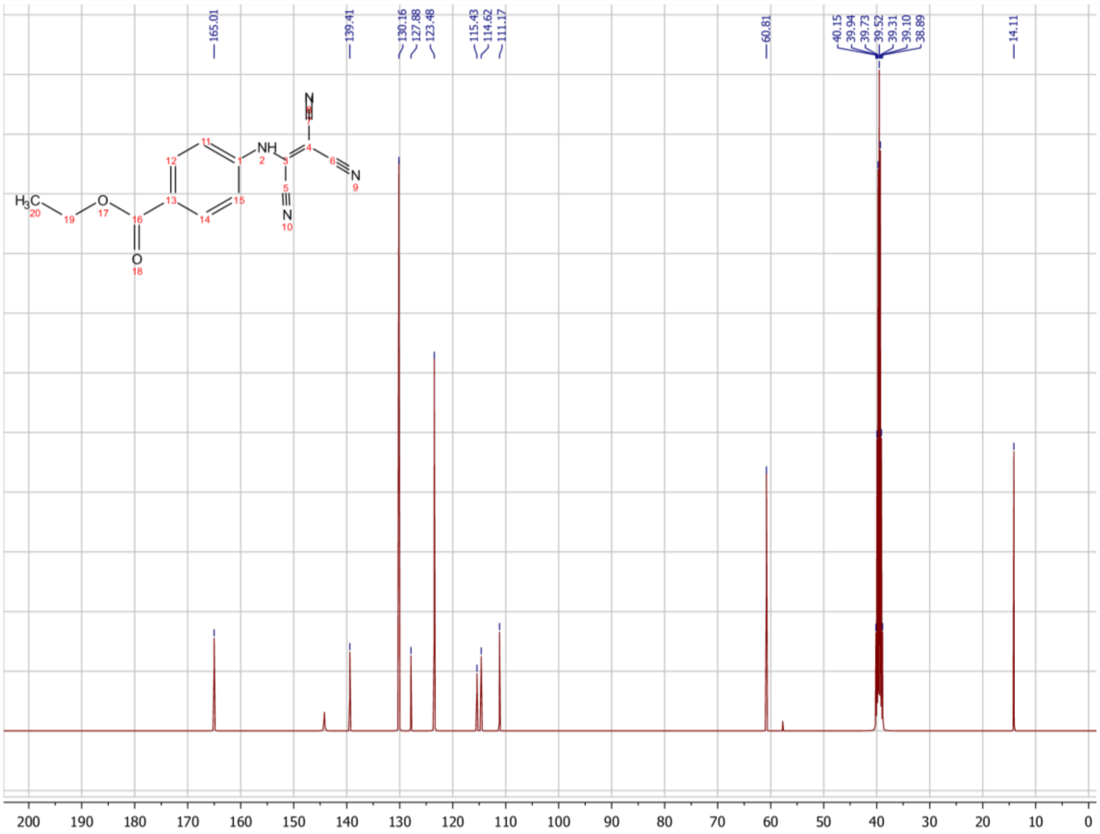

Figure S6. ^{13}C NMR spectrum of **5a** (100 MHz, DMSO-d$_6$, 298 K)

Figure S7. ^{1}H NMR spectrum of **5b** (400 MHz, DMSO-d$_6$, 298 K)

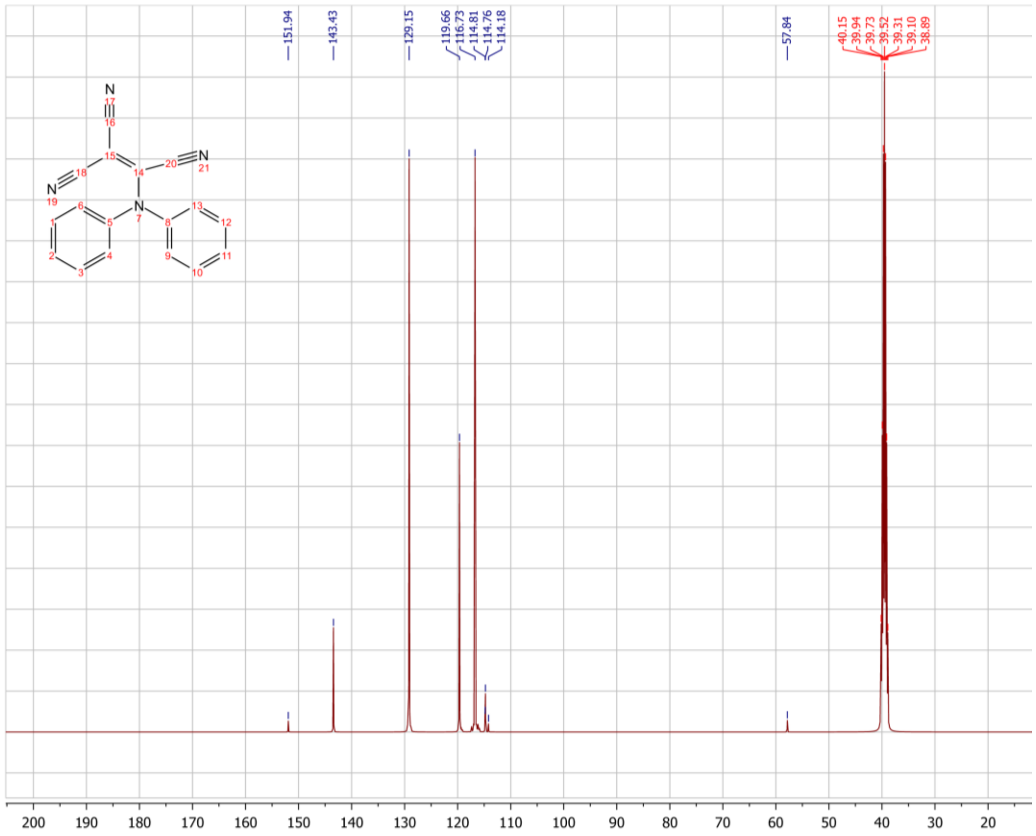

Figure S8. ^{13}C NMR spectrum of **5b** (100 MHz, DMSO-d$_6$, 298 K)

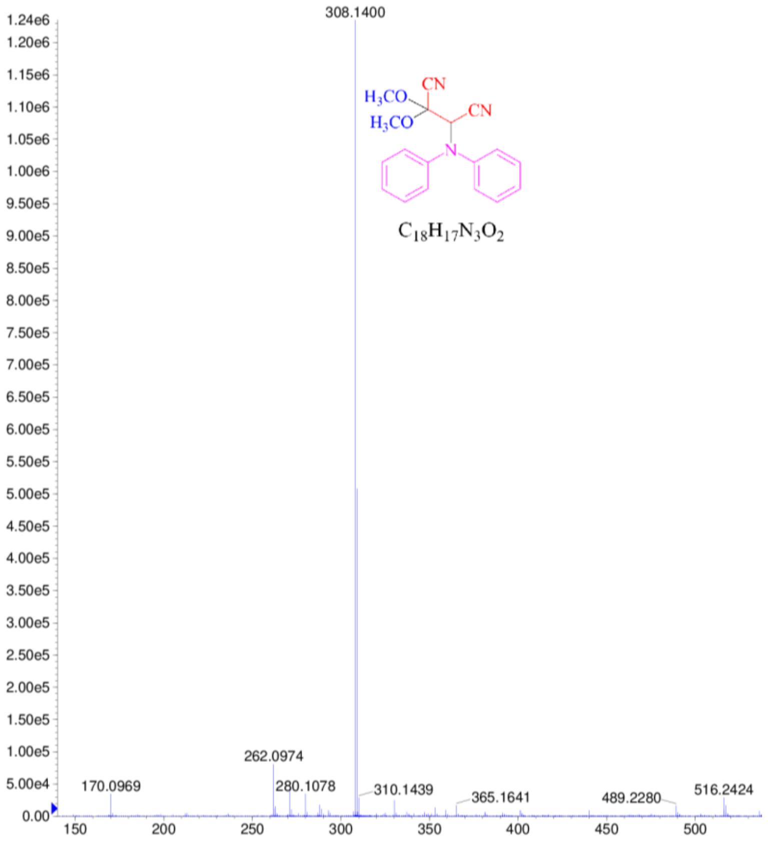

Figure S9 MASS spectrum of **5'b**

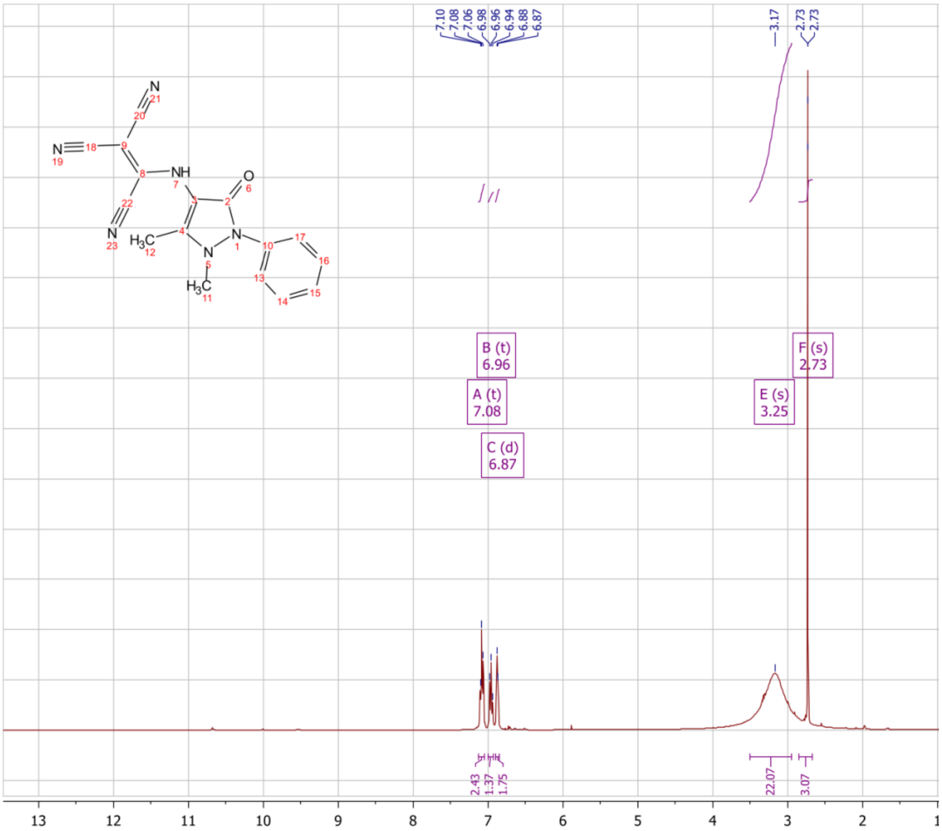

Figure S10. ^{1}H NMR spectrum of **5c** (400 MHz, DMSO-d$_6$, 298 K)

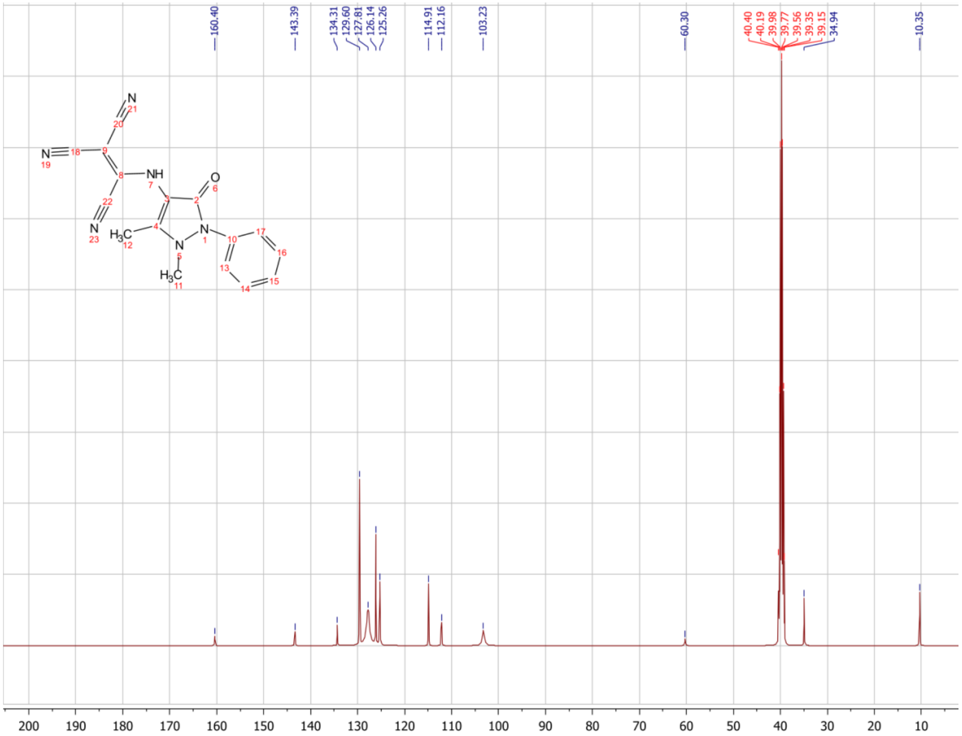

Figure S11. ^{13}C NMR spectrum of **5c** (100 MHz, DMSO-d$_6$, 298 K)

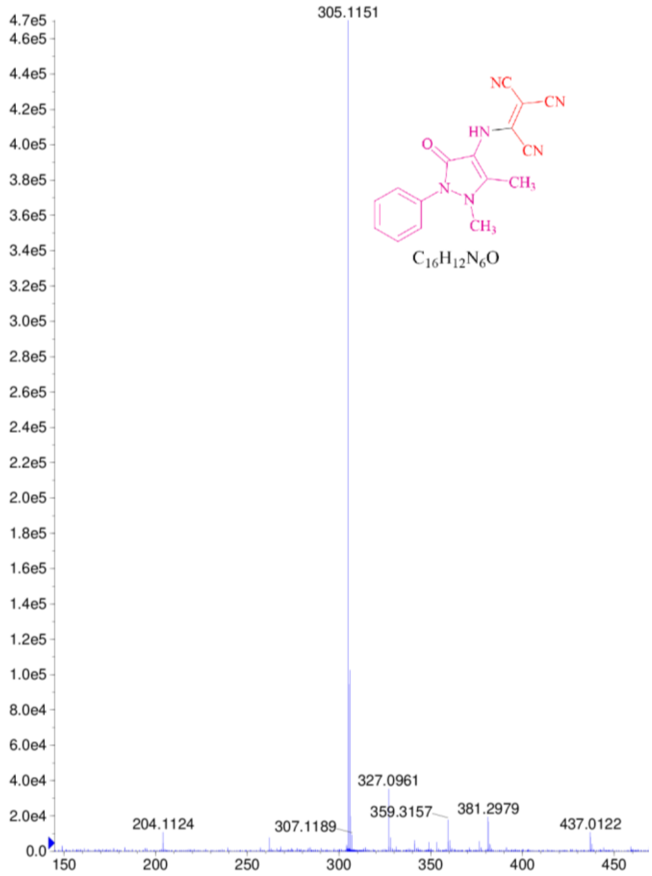

Figure S12. MASS spectrum of **5c**

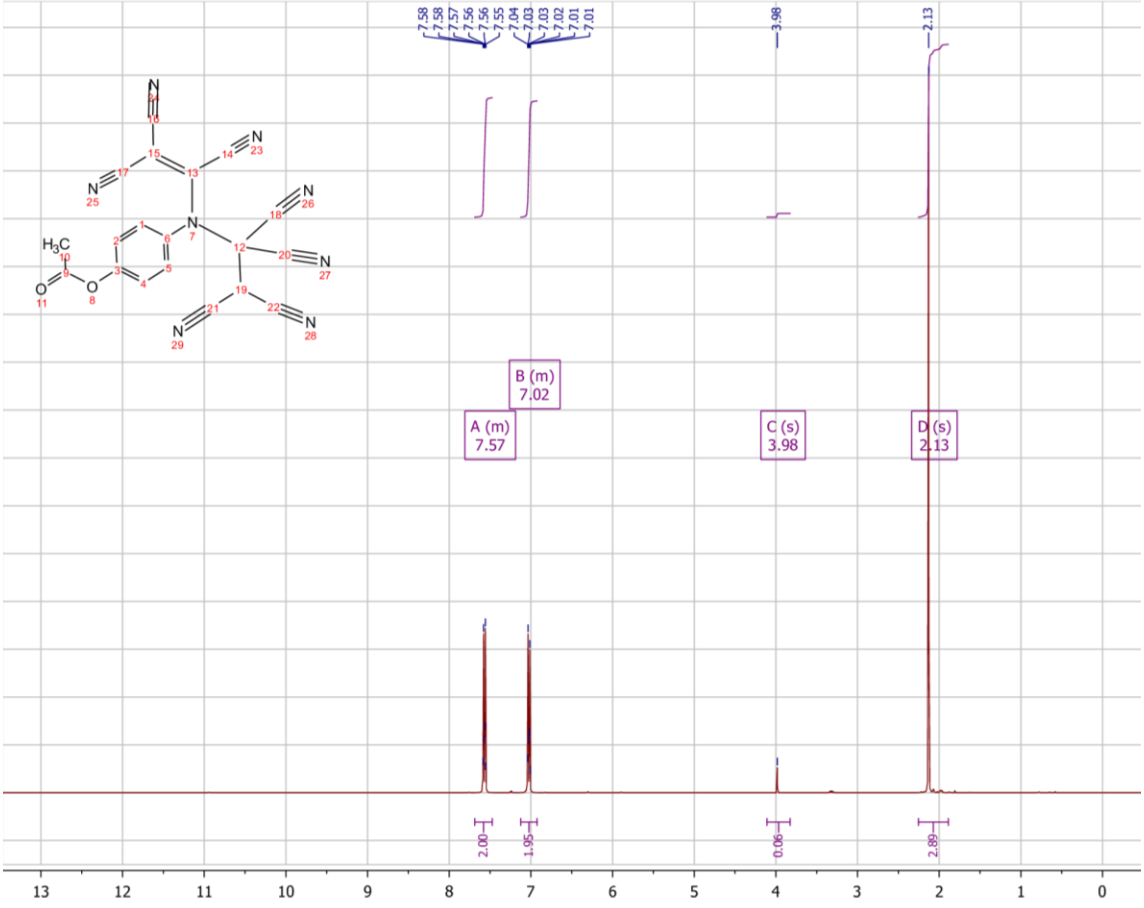

Figure S13. ^{1}H NMR spectrum of **6** (400 MHz, DMSO-d$_6$, 298 K)

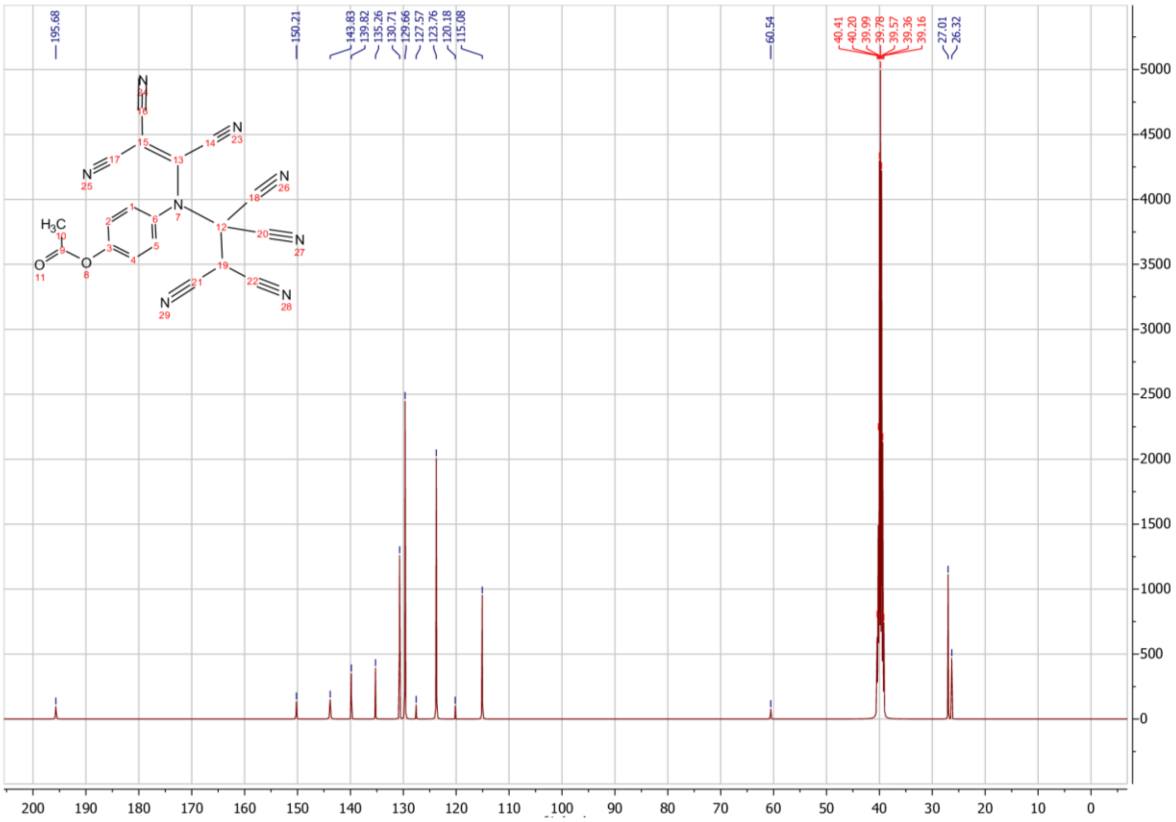

Figure S14. ^{13}C NMR spectrum of **6** (400 MHz, DMSO-d$_6$, 298 K)

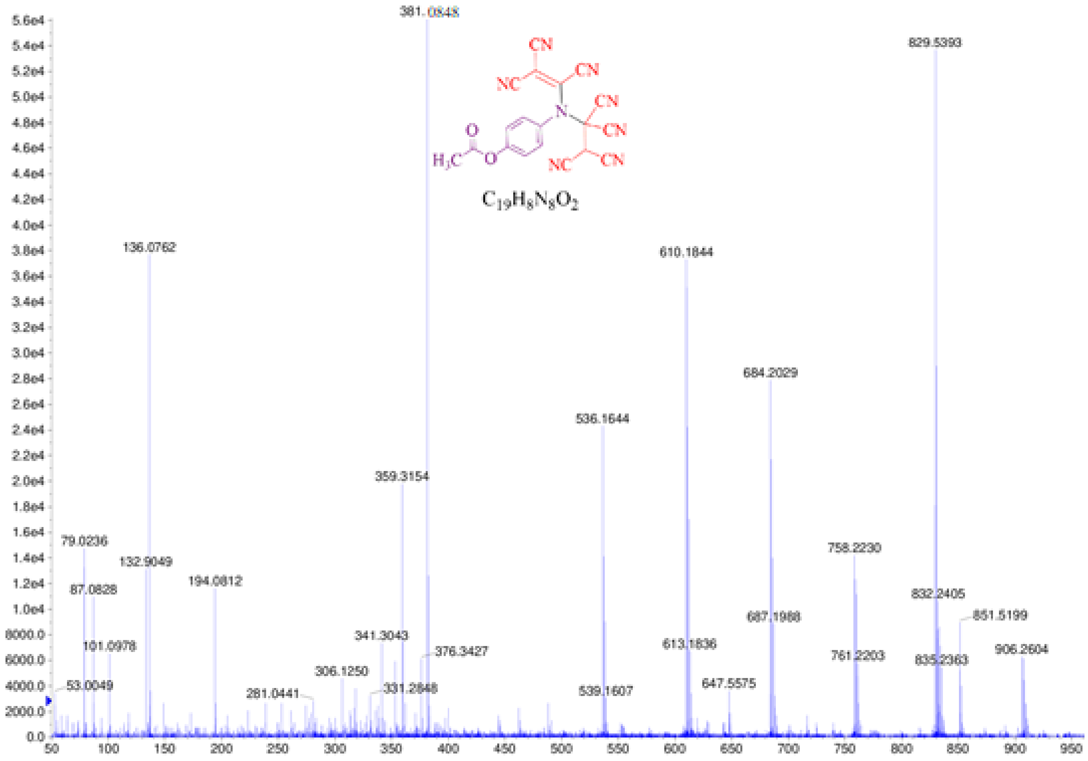

Figure S15. MASS spectrum of **6**